

Japanese Unexamined Patent Application
First Publication (A) No. S60-251924

First Publication Date: December 12, 1985
 Int. Cl.⁴: B 01 F 17/52, C 08 F 220/56, and C 08 F 220/58

Application No.: S59-106469
 Filing Date: May 28, 1984
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Specification

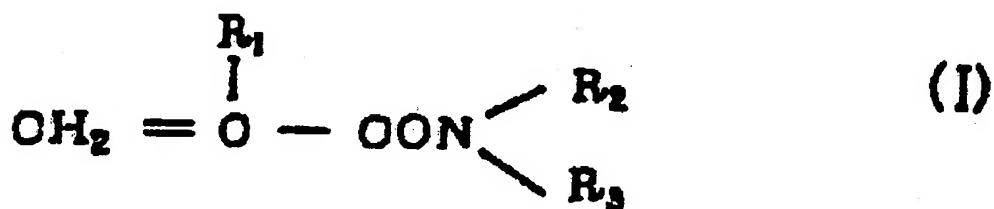
1. Title of the Invention

Polymer Surfactant

2. Claims

(1) A polymer surfactant comprising a homopolymer or copolymer of an N-alkyl or N-alkylene substituted (meth)acrylamide represented by general formula (I) or general formula (II):

General formula (I)



wherein R₁ represents a hydrogen atom or a methyl group; R₂ represents a hydrogen atom, a methyl group, or an ethyl group;

and R₃ represents a methyl group, an ethyl group, or a propyl group;

General formula (II)



wherein R₁ represents a hydrogen atom or a methyl group; and A represents $-(-\text{CH}_2-)_n-$ wherein n represents 4 to 6, or $-\text{O}(-\text{CH}_2-)_2-$

or a copolymer thereof with another copolymerizable monomer(s).

3. Detailed Description of the Invention

The present invention relates to a polymer surfactant, and more particularly relates to a polymer surfactant comprising a specific N-substituted (meth)acrylamide polymer.

Prior Art and Problems Thereof

Surfactants are conventionally employed in various fields such as cleansing, and the utility thereof is widely accepted. However, recently, various problems caused by use of surfactants have been occurring. One of these is a problem in foaming of waste fluid.

In addition, as one of recent new separation techniques, there is a technique for separation using liquid membranes. Among these, investigations regarding emulsified liquid membranes, focused on a double micelle structure, have been carried out. Even in this case, there are substantial

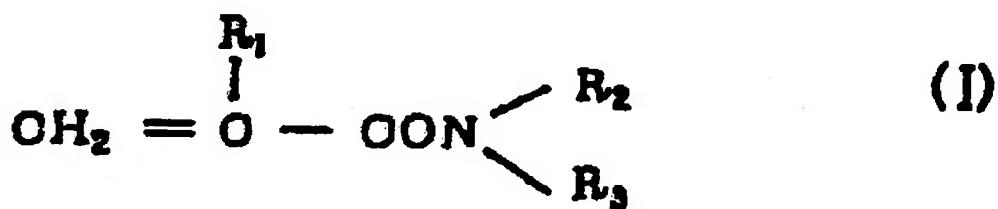
difficulties in deemulsification for destroying micelles. At present, deemulsification based on applying voltage has been investigated. However, a large amount of energy is consumed when doing this, and deemulsification is not satisfactory.

Means for Solving the Problems

As a result of investigations on various compounds focusing on change in surface tension according to temperature changing, which is one of the big factors in surface action, in view of the problems described above, the present inventors discovered that in an aqueous solution of a specific (meth)acrylamide polymer, change in surface tension varies greatly corresponding to temperature change, and surface activity can be controlled based on temperature, thus completing the present invention.

That is, the present invention relates to a polymer surfactant comprising a homopolymer or copolymer of an N-alkyl or N-alkylene substituted (meth)acrylamide represented by general formula (I) or general formula (II):

General formula (I)



wherein R₁ represents a hydrogen atom or a methyl group; R₂ represents a hydrogen atom, a methyl group, or an ethyl group; and R₃ represents a methyl group, an ethyl group, or a propyl group;

General formula (II)



wherein R₁ represents a hydrogen atom or a methyl group; and A represents $-(-\text{CH}_2-)_n-$ wherein n represents 4 to 6, or $-(-\text{CH}_2-)_2-$ $\text{O}-(-\text{CH}_2-)_2-$,

or a copolymer of the aforementioned monomer with another copolymerizable monomer(s).

As examples of the specific N-alkyl or N-alkylene substituted (meth)acrylamide of the present invention, mention may be made of, for example, N-n-propylacrylamide, N-n-propylmethacrylamide, N-isopropylacrylamide, N-isopropylmethacrylamide, N-ethylacrylamide, N,N-diethylacrylamide, N-ethylmethacrylamide, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, N-acryloylpyrrolidine, N-methacryloylpyrrolidine, N-acryloylpiperidine, N-methacryloylpiperidine, N-acryloylmorpholine, and the like.

In addition, as examples of monomers copolymerizable with the aforementioned monomer, mention may be made of hydrophilic monomers, ionic monomers, lipophilic monomers, and the like. One or more types of monomers described above can be employed. As detailed examples of hydrophilic monomers, mention may be made of, for example, acrylamide, methacrylamide, N-methylacrylamide, diacetoneacrylamide, hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, various methoxy polyethylene glycol methacrylates, various methoxy polyethylene glycol acrylates,

N-vinyl-2-pyrrolidone, and the like. In addition, vinyl acetate, glycidyl methacrylate, or the like may be introduced by copolymerization, the obtained product is subjected to hydrolysis, and thereby hydrophilic properties can also be provided. As examples of ionic monomers, mention may be made of, for example, acids such as acrylic acid, methacrylic acid, vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, 2-acrylamide-2-phenylpropanesulfonic acid, 2-acrylamide-2-methylpropanesulfonic acid, and the like, and salts thereof, amines such as N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminopropyl methacrylamide, N,N-dimethylaminopropyl acrylamide, and the like, and salts thereof, and the like. In addition, various acrylates, methacrylates, acrylamides, methacrylamides, acrylonitriles, and the like may be introduced by copolymerization, the obtained products are subjected to hydrolysis, and thereby ionic properties can also be provided. As examples of lipophilic monomers, mention may be made of, for example, N-alkyl (meth)acrylamide derivatives such as N-n-butylacrylamide, N-n-butylmethacrylamide, N-tert-butylacrylamide, N-tert-butylmethacrylamide, N-n-hexylacrylamide, N-n-hexylmethacrylamide, N-n-octylacrylamide, N-n-octylmethacrylamide, N-tert-octylacrylamide, N-n-dodecylacrylamide, N-n-dodecylmethacrylamide, and the like, N-(omega-glycidoxylalkyl) (meth)acrylamide derivatives such as N,N-diglycidylacrylamide, N,N-diglycidylmethacrylamide, N-(4-glycidoxylbutyl)acrylamide, N-(4-glycidoxylbutyl)methacrylamide, N-(5-glycidoxypentyl)acrylamide, N-(6-glycidoxylhexyl)acrylamide, and the like, (meth)acrylate derivatives such as ethyl acrylate, methyl methacrylate, butyl methacrylate, butyl acrylate, lauryl acrylate, 2-ethylhexyl methacrylate, glycidyl methacrylate, and the like, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, olefins such as ethylene, propylene, butene, 34

and the like, styrene, alpha-methylstyrene, butadiene, isoprene, and the like.

As a method for producing a polymer surfactant by polymerizing the aforementioned monomer, there is (1) a method in which polymerization is carried out in an aqueous solution, and thereby, the aqueous solution of the polymer is obtained as it is, or water is removed therefrom to thereby obtain a polymer solid; (2) a method in which polymerization is carried out in a solvent, and thereby, the solution of the polymer is obtained as it is, or the solvent is removed therefrom to thereby obtain a polymer, or alternatively the solution is added to a poor solvent which does not solve the polymer to thereby precipitate the polymer; (3) a method in which a polymer is obtained as a polymer emulsion by emulsification polymerization; (4) a method in which polymer particles are obtained by suspension polymerization; (5) a method in which the monomer is polymerized without dilution using a solvent, as a polymer block; and the like. Among these methods, methods (1), (2), and (3) are preferable.

In the aforementioned method (2), as the solvent employed during polymerization, various types of solvents can be employed since the (meth)acrylamide and the N-substituted derivatives thereof exhibit superior compatibility with respect to various solvents. As detailed examples of the solvents, mention may be made of alcohols such as methanol, ethanol, and the like, cyclic ethers such as tetrahydrofuran, 1,4-dioxane, and the like, ketones such as acetone, and the like, amides such as N,N-dimethylformamide, N,N-dimethylacetamide, and the like, aromatic hydrocarbons such as benzene, toluene, and the like, halogenated hydrocarbons such as chloroform, methylene dichloride, and the like, dimethylsulfoxide, N-methylpyrrolidone, chain-like glycols such as diglyme,

tetraglyme and the like, basic solvents such as pyridine, and the like, and the like.

During polymerization, as a method for initiating polymerization, the polymerization may be carried out by simply heating. When a polymerization initiator is employed, better results can usually be obtained.

The polymerization initiator is not particularly limited as long as it exhibits the capacity to initiate radical polymerization. For example, examples thereof include inorganic peroxides, organic peroxides, combinations between the aforementioned peroxides and reductants, azo compounds, and the like. As detailed examples thereof, mention may be made of ammonium persulfate, potassium persulfate, hydrogen peroxide, tert-butyl peroxide, benzoyl peroxide, cumene hydroperoxide, tert-butyl peroxy-2-ethylhexanoate, butyl perbenzoate, and the like. As examples of the reductants to be combined therewith, mention may be made of sulfites, bisulfites, salts having low degree of ionic valency of iron, copper, cobalt, or the like, organic amines such as aniline and the like, reduced sugars such as aldose, ketose, and the like, and the like. As the azo compounds, azobisisobutyronitrile, 2,2'-azobis-2-amidinopropane hydrochloride, 2,2'-azobis-2,4-dimethylvaleronitrile, 4,4'-azobis-4-cyanovaleic acid, and the like can be employed. In addition, two or more types of the aforementioned polymerization initiators can be employed together. The blending amount of the polymerization initiators in this case is sufficient in the quantitative range which is commonly employed, and for example, ranges from 0.01 to 5% by weight per monomer, and preferably ranges from 0.05 to 2% by weight.

Among these, a water-soluble polymerization initiator is preferable, and in particular, an ionic polymerization initiator which dissociates into ions in an aqueous solution is

preferable. The polymerization temperature ranges from 0 to 100°C, and preferably ranges from 5 to 80°C.

The polymers obtained as described above can be provided as powders by pulverizing solid polymers into powders or can be provided as a solution by dissolving them in any solvent, such as an aqueous solution. In addition, in the case of emulsions or particles, they can also be provided as they are.

The resins produced in accordance with the methods described above become hydrophobic as represented by dull deposit at a specific temperature when they are heated in an aqueous solution. At this time, surface tension is also decreased. Such a decrease is also observed in common surfactants, but the decreasing rate is small. For example, in the case of sodium lauryl sulfate, a difference in surface tension caused by a temperature difference of 30°C is at most 2 dyn/cm. In contrast, in the case of the present invention, the difference in surface tension caused by a temperature difference of 40°C ranges from 5 to 20 dyn/cm. Therefore, by selecting type and concentration of resin, the difference can be controlled. The concentration of the aqueous solution of the polymer ranges from 10 to 0.001% in the aforementioned case, and any concentration can be selected. Further convenience is in that the value of surface tension during heating is in the range of from 35 to 50 dyn/cm, which causes surface activation.

In addition, in general, when the polymer is hydrophobic, surface tension is decreased; and when the polymer is hydrophilic, surface tension is increased.

Therefore, by utilizing a large change of surface tension caused by temperature change, emulsification can be carried out at high temperature and deemulsification can be carried out at low temperature. Therefore, emulsification and

deemulsification can be controlled based on temperature difference.

In addition, various surfactants, various water-soluble polymers such as polyacrylates, aromatic sulfonates such as naphthalene sulfonate, various builders, and the like can be employed together with the resins described above. For example, in the case of employing a surfactant together with the resin, surface tension is decreased by heating, but surface tension may be increased starting at a specific temperature. The specific temperature varies depending on a combination of the resin and the surfactant. For example, in the case of a combination of poly-N-acryloylpiperidone and sodium lauryl sulfate, the specific temperature ranges from 40 to 60°C.

As described above, the surface tension in an aqueous solution of the polymer surfactant of the present invention can be controlled based on temperature and addition of the surfactant and the like.

As a detailed mode for carrying out the present invention, when an aqueous solution of the polymer surfactant of the present invention is heated and stirred, strong foaming is observed, and during the strong foaming, an oil substance is added and thereby a water-in-oil emulsion can be formed. An oil-in-water emulsion can be produced by increasing the amount of the oil component. At this time, the emulsified state can be maintained at the current temperature. Subsequently, deemulsification can be carried out, when the emulsion is cooled. In the case of employing a common surfactant, during deemulsification, even after the aqueous layer and the oil layer are separated, it is difficult to lose micelles in the oil layer. In contrast, in the case of employing the surfactant of the present invention, it is easy to lose micelles both in the oil layer and in the aqueous layer, and there are no problems although a small amount of micelles may

remain at the interface. As the oil substance, aliphatic hydrocarbons of petroleum type, aromatic hydrocarbons such as styrene, lipophilic monomers such as methyl methacrylate, N-n-butylacrylamide, and the like can be employed. Emulsification may be sufficiently carried out by means of a stirrer such as a propeller type stirrer, and more preferably a high-speed stirrer such as a homomixer.

Operation

The polymer surfactant of the present invention has surface activity which varies depending on temperature. Therefore, it may be applied in the field of moisturizing agents, penetrating agents, foaming agents, emulsifiers, dispersing agents, dissolving agents, cleansing agents, smoothing agents, antistatic agents, lubricants for use in metals, rust preventive agents, leveling dyeing agents, hydrophobicating agents, fungicides, coagulating agents, and the like, in which surfactants are conventionally employed.

The polymer surfactant of the present invention exhibits effects in which (1) functions of the surfactant such as emulsification can be controlled based on temperature; (2) the destroying of micelles can be easily carried out, and for this reason, separation of water and oil can be carried out thoroughly; (3) surface activity can be controlled based on the composition of the polymer and addition of various additives; and the like.

Example 1

150 g of N-acryloylpyrrolidine was dissolved in 655 g of distilled water, and the solution was cooled to 10°C. Subsequently, it was placed in a Dewar Vessel bottle made of stainless steel with a volume of 1 liter, and bubbling of a nitrogen gas was carried out by means of a ball shaped filter

in a flowing amount of 0.5 L/min. Subsequently, to the aforementioned aqueous solution, a solution in which 0.8 g of ammonium persulfate was dissolved in 10 g of distilled water and a solution in which 0.34 g of sodium bisulfite was dissolved in 10 g of distilled water were simultaneously added, to thereby polymerize the aforementioned aqueous solution in a heat-insulating manner, thus producing a 20% aqueous solution of a polymer of N-acryloylpyrrolidine. Surface tension of an aqueous solution in which the aforementioned aqueous solution of the polymer was diluted with distilled water to have a concentration of 0.05% was measured at each of various temperatures by means of a tensiometer. The results were that surface tension was 63.2 dyn/cm at 20°C; 61.1 dyn/cm at 40°C; and 56.8 dyn/cm at 60°C.

Examples 2 to 6

The 20% aqueous solution of N-acryloylpyrrolidine obtained in Example 1 was diluted with distilled water to the concentrations shown in Table 1, to thereby obtain aqueous solutions. Using the obtained aqueous solutions, surface tension thereof at each of various temperatures was measured in the same manner as in Example 1. The results are shown in Table 1.

Examples 7 to 17

The 20% aqueous solution of N-acryloylpyrrolidine obtained in Example 1 was diluted with distilled water to the concentrations shown in Table 2, to thereby obtain aqueous solutions. In addition, using an aqueous solution into which sodium lauryl sulfate was added and dissolved, to thereby have the concentrations shown in Table 2, surface tension thereof at each of various temperatures was measured in the same manner as in Example 1. The results are shown in Table 2.

Comparative Example 1

In the same manner as in Example 1, surface tension of an aqueous solution of sodium lauryl sulfate in a concentration of 0.01 mol/l at each of various temperatures was measured. The results were that surface tension was 42.6 dyn/cm at 40°C; 40.9 dyn/cm at 60°C; and 40.4 dyn/cm at 70°C.

Examples 18 to 31

In the same manner as in Example 1, 20% aqueous solutions of the polymer having copolymerization compositions shown in Table 3 were obtained. The obtained aqueous solutions were diluted with distilled water to the concentrations shown in Table 3. In the same manner as in Example 1, surface tension thereof at each of various temperatures was measured. The results are shown in Table 3.

Table 1

Example	Concentration of N-acryloylpyrrolidine polymer (% by weight)	Surface tension (dyn/cm)			
		2°C	20°C	40°C	60°C
2	0.1	67.6	63.0	60.0	56.2
3	0.5	-	63.0	59.1	55.8
4	1.0	-	63.0	58.8	55.8
5	5.0	-	62.4	58.7	55.4
6	10.0	-	60.2	58.0	55.0

Table 2

Example	Concentration of N-acryloylpyrrolidine polymer (% by weight)	Concentration of sodium lauryl sulfate (mol/L)	Surface tension (dyn/cm)				
			2°C	20°C	40°C	60°C	70°C
7	0.05	0.00001	-	61.4	55.1	51.7	-
8	0.05	0.0001	-	57.1	50.7	49.2	-
9	0.05	0.001	-	41.9	39.5	40.5	-
10	5.0	0.000001	-	61.4	58.4	56.4	-
11	5.0	0.00001	-	62.9	59.4	56.4	54.0
12	5.0	0.00005	58.5	55.4	53.0	53.5	-
13	5.0	0.0001	54.5	52.0	50.6	52.8	54.5
14	5.0	0.0005	45.8	43.9	43.4	49.2	-
15	5.0	0.001	-	40.3	40.4	45.9	-
16	5.0	0.0025	-	40.3	38.9	40.3	-
17	5.0	0.005	-	42.4	42.0	42.0	-

Table 3

Example	Copolymerization composition *1) (%; % by weight)	Concentration of aqueous solution (% by weight)	Surface tension (dyn/cm)			
			2°C	20°C	40°C	60°C
18	N-EtAAM (100)	0.1	67.5	63.3	59.6	56.0
19	N-PrAAM (100)	0.1	52.4	46.3	40.7	39.3
20	N-PrAAM (100)	1.0	49.7	45.0	43.0	-
21	N-AcPi (100)	0.1	52.4	48.6	47.3	45.9
22	N-AcPy (12.5) / N-PrAAM (87.5)	0.1	55.8	50.0	44.1	41.8
23	N-AcPy (25) / N-PrAAM (75)	0.1	56.9	50.5	45.5	43.0
24	N-AcPy (50) / N-PrAAM (50)	0.1	56.5	51.0	47.3	44.5
25	N-AcPy (85) / N-BuAAM (15)	0.1	60.1	55.5	50.8	47.6
26	N-AcPy (25) / N-AcPi (75)	0.1	60.3	55.4	50.0	47.3
27	N-AcPy (50) / N-AcPi (50)	0.1	62.4	56.9	51.9	48.2
28	N-AcPy (75) / N-AcPi (25)	0.1	66.1	61.0	56.9	52.8
29	N-AcPi (90) / AANa (10)	0.1	61.0	56.0	50.8	47.6
30	N-AcPi (90) / APPSNa (10)	0.1	60.1	54.7	50.0	47.3
31	N-AcPi (90) / APPSNa (10)	5.0	56.7	49.0	43.7	42.8

*1) N-EtAAM = N-ethylacrylamide; N-PrAAM = N-n-propylacrylamide; N-AcPy = N-acryloylpiperidine; N-AcPy = N-acryloylpiperidine; N-BuAAM = N-n-butylacrylamide; AANa = sodium acrylate; APPSNa = sodium 2-acrylamido-2-phenylpropanesulfonate

Example 32

Sodium alpha-naphthalene sulfonate was added to the 0.1% polymer solution obtained in Example 23 so that the

concentration thereof was 1%, and was dissolved. Using the solution, in the same manner as in Example 1, surface tension thereof at each of various temperatures was measured. The results were that surface tension was 57.4 dyn/cm at 2°C; 51.9 dyn/cm at 20°C; 46.8 dyn/cm at 40°C; and 43.6 dyn/cm at 60°C.

Examples 33 to 37

Two types of aqueous polymer solutions were mixed in the ratios shown in Table 4. Using the aqueous solutions, in the same manner as in Example 1, surface tension thereof at each of various temperatures was measured. The results are shown in Table 4.

Table 4

Example	Mixture composition *1) (); % by weight		Surface tension (dyn/cm)			
	First aqueous solution	Second aqueous solution	2°C	20°C	40°C	60°C
33	0.1%-poly(N-AcPy) (25)	0.1%-poly(N-PrAAM) (75)	54.1	48.0	42.4	41.7
34	0.1%-poly(N-AcPy) (50)	0.1%-poly(N-PrAAM) (50)	55.0	48.7	42.7	40.8
35	0.1%-poly(N-AcPy) (75)	0.1%-poly(N-PrAAM) (25)	57.4	50.8	44.6	42.0
36	1%-poly(N-PrAAM) (75)	1%-poly(AANH ₄) (25)	48.7	43.5	41.6	-
37	1%-poly(N-AcPy) (75)	1%-poly(AANH ₄) (25)	59.1	53.0	48.3	-

*1) AANH₄ = ammonium acrylate

Example 38

The 20% aqueous solution of N-n-propylacrylamide obtained in Example 19 was diluted with distilled water to thereby produce a 0.25% aqueous solution. 100 ml of styrene was added to 400 ml of the aforementioned aqueous solution, and the

mixture was stirred for 10 minutes at 60°C at 4000 rpm by means of a homomixer, thus producing an emulsion.

The emulsion was cooled to 20°C. As a result, this separated into a styrene layer and an aqueous layer, and both layers were transparent.

Comparative Example 2

An emulsion was obtained in the same manner as in Example 38, with the exception of using a 0.25% aqueous solution of sodium lauryl sulfate instead of the 0.25% aqueous solution of the polymer of N-n-propylacrylamide. The aforementioned emulsion was cooled to 20°C. As a result, this separated into a styrene layer and an aqueous layer. The aqueous layer was transparent, but the styrene layer remained as it was when emulsified.

Amendments

April 30, 1985 (Showa 60)

1. Identification of the Case

Application No. S59-106469

2. Title of the Invention

Polymer Surfactant

3. Entity Effecting Amendments

Relationship Applicant

Name Mitsui Toatsu Chem. Inc.

4. Number of Inventions Increased by the Amendments

0

5. Object of the Amendments

Section of "Detailed Description of the Invention"
of the Specification

6. Contents of the Amendments

1) "655 g" described in lines 5 and 6 of page 14 of the Japanese Specification (see *Example 1, the first line*) is amended to "580 g".

2) The following Examples are added after line 10 of page 21 of the Japanese Specification (see the last line of the Specification).

"Example 39

A 20% aqueous solution of a polymer of N-isopropylacrylamide was obtained in the same manner as in Example 1, with the exception of employing N-isopropylacrylamide instead of N-acryloylpiperidone. The aforementioned aqueous solution of the polymer was diluted with distilled water to a concentration of 0.1%. Using this aqueous solution, surface tension thereof was measured at each of various temperatures in the same manner as in Example 1. The results were that surface tension was 53.1 dyn/cm at 2°C; 48.2 dyn/cm at 20°C; 42.5 dyn/cm at 40°C; and 41.2 dyn/cm at 60°C.

Example 40

A 30% N,N-dimethylformamide solution of N,N-diethylacrylamide was placed in a Dewar vessel bottle, and the solution was subjected to nitrogen replacement. Subsequently, 1.5% of azobisisobutyronitrile was added to the solution at 30°C, to thereby polymerize the mixture in a heat-insulating manner. The obtained gel was cut into small pieces, followed by drying under a vacuum at 60°C. Subsequently, the dried product was pulverized into powders. The aforementioned powders were dissolved in distilled water to thereby obtain a 0.1% aqueous polymer solution of N,N-diethylacrylamide. Using this aqueous polymer solution, in the same manner as in Example 1, surface tension thereof at each of various temperatures was measured. The results were that surface tension was 60.2 dyn/cm at 2°C; 55.4 dyn/cm at 20°C; 51.3 dyn/cm at 40°C; and 47.8 dyn/cm at 60°C.

Example 41

A 20% aqueous solution of a polymer of N-acryloylmorpholine was obtained in the same manner as in Example 1, with the exception of employing N-acryloylmorpholine instead of N-acryloylpyrrolidine. The aforementioned aqueous solution of the polymer was diluted with distilled water to a concentration of 0.1%. Using this aqueous solution, surface tension thereof was measured at each of various temperatures in the same manner as in Example 1. The results were that surface tension was 52.6 dyn/cm at 2°C; 48.9 dyn/cm at 20°C; 47.5 dyn/cm at 40°C; and 46.1 dyn/cm at 60°C."